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DARPA R&D Status Report

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Principal Investigator: James Cella

DISTRIBUTION STATEMENT A

Approved for public release;
Distribution Unlimited

Telephone No.: (518) 387-6173/(518) 387-7342

Short Title of Work: Non-toxic, Self Cleaning Silicone Foul Release Coatings

Reporting Period: October through December 1997

Description of Progress:

Task 1: Design , synthesis and testing of foul release paints with improved antifouling and release properties

Task 1.1: Design, synthesis and testing of foul release paints (GE-CRD)

Data collection continues on about 50 screening panels at FIT, and about 70 panels at MMRTS. A set of downselected compositions was deployed by the subcontractors in July 1997. A set of bilge keel panels is in preparation. We are in the planning stage for the next set of downselect panels.

Task 1.1.1: Quantitative foul release performance of new materials (FIT)

Static Immersion of Test Coatings

The test coatings are applied to screening panels (4" x 10") for short term evaluation and down select panels (10" x 12") for long term appraisal. A total of 130 screening panels have been exposed to barnacle fouling at the Florida Institute of Technology static immersion site since January 1997 (Table 1). These were caged to prevent loss of barnacles by fish predation. Fifty of these were removed on 12 November 1997. We

have obtained 3,844 barnacle adhesion measurements. A total of 28 down select panels were placed under static immersion (7/17/97). All the coatings were water jetted on 8/21/97. A second water jet evaluation will take place on 1/21/98. A total of 1,074 barnacle adhesion measurements have been taken on 9/19/97 and 11/16/97.

Table I Status of Test Panels 1 January 1998
 Q = Q Panels; DS = Down Select Panels

Start Date	Panel Type	No. Panels	Barn Adh. Measure	No. of Time Series
1/22/97	Q	20	3071	5
3/25/97	Q	24	467	2
5/2/97	Q	21	262	2
7/17/97	DS (fouling)	28	1074	1
7/18/97	Q	6	10	1
8/15/97	Q	5	26	1
9/9/97	DS (foil tests)	14	0	0
9/10/97	Q	2	8	0

Development of the Skin Friction Measuring Device

A total of 14 down select panels have been immersed (9/9/97) specifically to address skin friction and hydrodynamic foul release as measured by an instrumented foil. Barnacle adhesion measurements have been obtained for the panels and foil testing will begin as soon as the weather cooperates.

Task 1.1.2: Field Exposure Testing (Bridger Scientific)

Fouling coverage and foul release/adhesion data obtained during the third quarter and the October 1997 inspections for the four preliminary and thirteen downselect formulations were presented at the 27 October program meeting. All panels were inspected again for fouling coverage and foul release (water jet) during November, 1997. Following the final evaluation and testing this season, panels were cleaned and re-immersed. This minimized coating damage by attached gastropods which are the primary foulers at most sites, and allows additional temporal adhesion data to be obtained in the Spring 1998. Evaluation and testing of the preliminary panels at the Manchester Street Station site (272 days exposure) was concluded due to substantial coating delamination, and abrasion/scarring by snails. These panels were removed, cleaned, photographed and returned to GE CRD.

Adhesion measurements (ASTM 5618) obtained this year for the preliminary and downselect coatings have been compiled and forwarded to the University of Hawaii and Florida Institute of Technology for further statistical analyses.

Based on the compiled seasonal information, and fouling/foul release data collected during the last inspections, all downselect coatings were given an overall performance

score. The panels breakdown into three general categories with the best class showing an insignificant amount of fouling and attached material is minimally adhesive.

Task 1.2: Validation testing (NSWC, University of Hawaii)

Bilge keels panels will be mounted on the John Paul Jones in January 1998. Panel preparation is currently underway at GE CRD.

Fouling of the experimental panels immersed at the Ford Island site had increased substantially over that present at the September inspection. All treatments except BRA were fouled to some extent, at least around the edges. The most heavily fouled compositions supported macrofouling on greater than 40% of the surface, while a second group supported fouling on 20%, a third group at 14% coverage, and the best performers were less than 10% fouled. No damage or coating failures were observed on any of the panels. Forces required to remove *Hydrodides* increased significantly from the September to the November sampling date, in some cases doubling. There remained significant differences among the panels in force required to remove *Hydrodides*. Trends in mean force to remove tubeworms were similar between the November and September sampling dates, despite the overall increase in force required for removal. Panels that performed well in terms of removal of tubeworms also performed well in tests on oysters.

Task 2: Optimize Coating Physical and Application Properties

Task 2.1 Physical property optimization (GE)

The storage modulus and $\tan \delta$ were obtained for the downselect compositions. There was no correlation between these bulk properties and the fouling release performance of the coatings. Panels have been sent to Dr. Irwin Singer at NRL for surface modulus measurements.

Task 2.2.1 Cleanability of foul release coatings (SUNY Buffalo)

Pre-exposure evaluations of the Down select #1 panels were completed.

Acid-base components using comprehensive contact angle data were calculated for the downselect compositions. Previous work indicated that surfaces having acid component values close to zero and relatively high base component values were likely to resist long term biological adhesion. The panels which exhibit the best overall performance to date have acid components close to zero but do not necessarily have high base components. If acid/base polarities are important predictors of short and/or long term biological adhesion, the relationship may not be linear.

Field evaluation of the downselected set #1 panels were conducted on November 13, 1997. Slime coverage varied from coating to coating. No zebra mussels were found on eight of the compositions.

Task 3: Environmental Impact and Toxicological Testing

Task 3.1: Environmental Impact (GE)

Metal strips coated with crosslinked RTV and ^{14}C -labeled polydimethylsiloxane (PDMS) have been aging in both fresh water and salt water tanks for nearly eight months. After seven months in both fresh water and salt water, less than 0.25% of the total ^{14}C was detected in the aqueous phase, and less than 0.05% of the total ^{14}C was detected in the sediment.

Similarly, metal strips coated with crosslinked RTV and ^{14}C -labeled poly(dimethyldiphenyl)siloxane (SF1154) have been suspended in both fresh water and salt water fish tanks for nearly seven months. After six months in both fresh water and salt water, less than 0.45% of the total ^{14}C was detected in the aqueous phase, and less than 0.05% was detected in the sediment.

Metal strips coated with crosslinked RTV and ^{14}C -labeled, carbinol terminated silicone oil have been aging in both fresh water and salt water tanks for nearly two months. After one month, approximately 1% of the total ^{14}C was detected in the aqueous phase in both fresh water and salt water fish tank systems.

A copy of a paper submitted to the Silicones in Coatings II Conference to be held March 1998 is provided.

Task 3.2: Toxicological Studies (NSWC, NCCOSC)

To date, nine coatings have been sent to SPAWAR Systems Center, San Diego for toxicity testing using the mysid shrimp, inland minnow, and a marine chain diatom. Of these coatings, all have been tested on the mysid shrimp, six have been tested on the chain diatom, and none have been tested on the minnow. This month we will continue our testing program with the minnows on all nine coatings. Chemical analysis on the leachates for all coatings is presently being conducted this month for DBT and TBT using purge and trap/ hydride derivatization followed by atomic absorption detection.

Change in Key Personnel:

None

Summary of Substantive Information Derived from Special Events

A team meeting was held in San Diego in October. An ONR review of navy antifouling efforts was attended by NSWC, NCCOSC, University of Hawaii, FIT, SUNY Buffalo, and GE-CRD.

Problems Encountered and/or anticipated:

None

Action required by the Goverment

None

Fiscal Status:

Project Cost:	\$931,135
Cost Share:	<u>(230,395)</u>
Net to ONR/DARPA:	\$700,740

Traditional antifouling paints containing toxic organotin or copper compounds are highly effective biofouling inhibitors; however, due to the introduction of toxins into the environment, the use of these types of antifouling agents is either prohibited or restricted. Low surface free energy silicone coatings have been introduced as an alternative to toxic paint in which the adhesive strength of attachment of biofoulers has been reduced. Although the silicone coatings do not completely prevent the attachment of biofouling organisms to surfaces, the fouling is easily removed by physical processes which include pressure washing or gentle scrubbing.

Some of the most effective silicone fouling release coatings contain 10-20% free oil. Although the mechanisms of enhanced foul release properties of these coatings are not well understood, it has been shown that attachment forces are lower on liquid-like layers relative to solid layers.¹ Several oils have been screened for their ability to enhance biofouling release properties including silicone oils of various functionality and polyethylene oxide containing oils. Barnacle adhesion measurements on fouling release coatings substantiate that removal of fouling requires less force when oils are incorporated into the network.² We have recently evaluated the fouling release properties of RTV, using RTV11[®] in which polydimethylsiloxane (PDMS, matrix compatible) and poly(dimethyldiphenyl)siloxane (PDMFPS, matrix-incompatible) oils have been incorporated. We have found that the fouling release behavior of compositions containing incompatible oils is greater than compositions which contain compatible oils. However, it is anticipated that incompatible oils may readily leach from the coatings. Depletion of the oil is anticipated to adversely affect biofouling release performance and would result in increased levels of silicones released to the environment.

In this paper, we report our results on the leachability of PDMS and PDMDPS from RTV11® in aqueous environments as a function of time.

Synthesis of ^{14}C -labeled oils

The leach rate of silicone oils from the silicone topcoat was readily determined using ^{14}C -labeled oils. Use of radiolabeled oils simplifies the analysis in studies of this type as all components of the matrix can be easily analyzed using radiometric detection (refer to Analysis section). The radiolabeled oils corresponded in composition to those employed in determination of the barnacle adhesion measurements.

All radiolabeled syntheses were performed by Wizard Laboratories, West Sacramento, California. The radiolabeled precursor to both the PDMS and PDMDPS oils consisted of a ^{14}C -labeled octamethylcyclotetrasiloxane (D_4) which was prepared by the reaction of tetrachlorotetramethylcyclotetrasiloxane with ^{14}C -labeled methyl Grignard reagent.

To prepare the radiolabeled PDMS, ^{14}C -D₄ was equilibrated with dodecamethylpentasiloxane using a strong-acid ion exchange resin (Figure 1). After 24 hours at 100 °C, there existed an equilibrium mixture of trimethylsiloxy capped dimethylsiloxy oligomers. Following removal of the catalyst, the PDMS oligomers were devolatilized for 2 hours at 200°C/0.1 mm Hg. By ^{29}Si NMR spectroscopy, the average dimethylsiloxy block length (x, Figure 1) was determined to be 149.

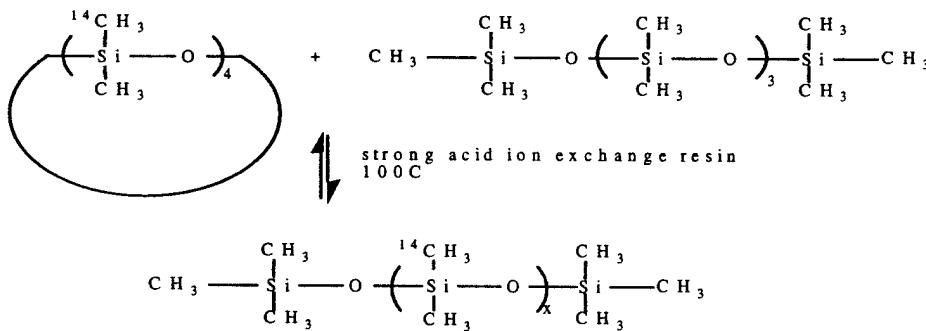


Figure 1 synthesis of ^{14}C -labeled PDMS

Similar methodology was utilized in the preparation of the radiolabeled PDMDS. Specifically, ^{14}C -D₄ was equilibrated with octaphenylcyclotetrasiloxane and dodecamethylpentasiloxane in the presence of a potassium trimethylsilanolate catalyst (Figure 2). Analysis of the ^{14}C -PDMDPS by ^{29}Si NMR spectroscopy indicated a dimethylsiloxy:diphenylsiloxy ratio of 46.7:53.3 (wt:wt), and the material contained 10.5 wt % trimethylsiloxy endgroups.

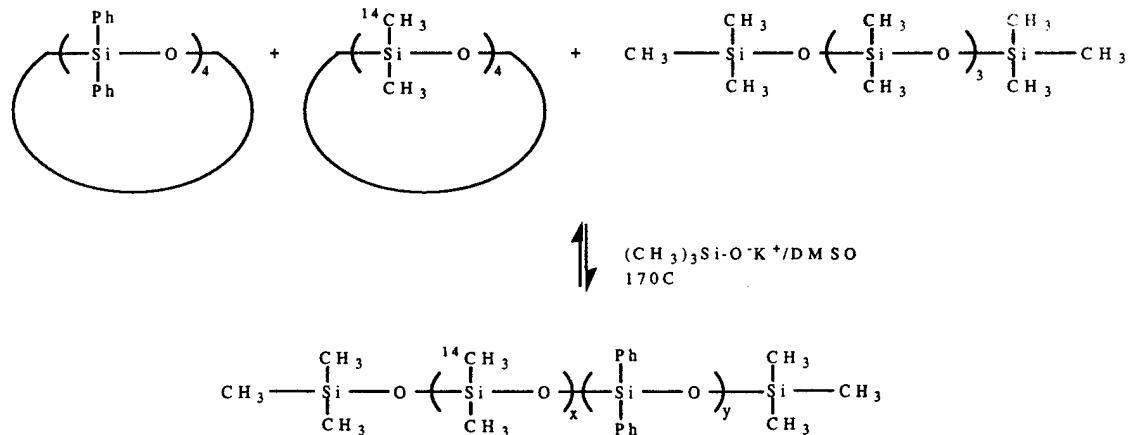


Figure 2 synthesis of ^{14}C -labeled PDMDPS

Preparation of silicone paint containing ^{14}C -labeled silicone oils

Aluminum strips coated with epoxy were weighed and then painted with a mixture of RTV11[®] (using dibutyltindilaurate at 0.5 wt % loading as the cure catalyst) and ^{14}C -labeled silicone oil (10 wt %). The RTV was allowed a 1 week cure time after which the aluminum strips were weighed to determine the total amount of silicone topcoat (RTV + oil) applied to each strip. Assuming a uniform distribution of ^{14}C -oil throughout the RTV, the amount of ^{14}C -oil in each panel was calculated. The panels were then soaked in water for several days to leach out the tin. The tin rinse water was analyzed for total ^{14}C by liquid scintillation analysis to account for any radiolabeled oil that leached into the water.

Experimental design

The painted aluminum strips were suspended in both salt and fresh water fish tanks containing marine and fresh water sediments, respectively (Figure 3). Marine sediment was obtained from Tampa Bay and fresh water sediment from the Scioto River, Columbus, Ohio. The pH of these sediments was 7.9 and 7.5, respectively. Three gallon glass fish tanks were utilized and each tank contained 6 liters of distilled water and 305.25 grams of the appropriate sediment (based on sediment dry weight). To the marine tanks was added 0.5 cup sea salts per gallon of water. Each tank contained 12 painted aluminum panels. The tanks were maintained in the dark, and the water was stirred from overhead to simulate movement of a boat through water.

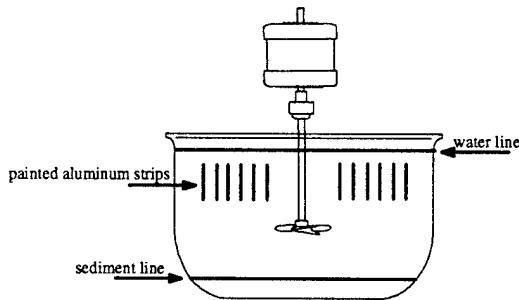


Figure 3 fish tank system design

Each month, 1 aluminum strip was removed from each of the 4 fish tanks (1 fresh water and 1 salt water tank for both of the ^{14}C -oils) and the amount of ^{14}C -labeled oil remaining in the RTV was determined by thermal oxidation. This process involved combusting 50-200 mg samples of the silicone topcoat in a Packard Model 307 sample oxidizer. Any ^{14}C -labeled oil was oxidized to $^{14}\text{CO}_2$, trapped in a liquid scintillation cocktail, and analyzed using a LKB-Wallac Model 1214 Rackbeta liquid scintillation counter. Based on the average of 3-5 samples per aluminum strip, the amount of ^{14}C -oil per gram of silicone topcoat was determined. The total amount of oil in each aluminum strip was then calculated based on the total weight of the silicone topcoat for a given aluminum strip. Each month, the amount of ^{14}C in the water and sediment was determined by liquid scintillation analysis and thermal oxidation/liquid scintillation analysis, respectively.

Results

After 5 months in both fresh water and salt water, <0.2% and $\leq 0.02\%$ of the total ^{14}C -PDMS was detected in the water and sediment, respectively. Mass balance data up to 5 months (Table 1) indicate that, on average, >99% of the theoretical amount of ^{14}C -PDMS remained in the silicone topcoat. The observation of >100% of the theoretical amount of ^{14}C -oil in several of the aluminum strips suggests that the ^{14}C -oil was not completely uniform throughout the RTV.

time (months)	system	% of total ^{14}C				
		in tin rinse	in water	in sediment	in RTV	total
1	PDMS fresh	0.05	0.05	0.01	100.03	100.14
2	"	0.05	0.07	0.01	101.54	101.67
3	"	0.05	0.13	0.01	100.74	100.93
4	"	0.05	0.13	0.01	101.82	102.01
5	"	0.05	0.16	0.02	96.08	96.31
1	PDMS salt	0.05	0.04	0.02	95.31	95.42
2	"	0.05	0.07	0.01	105.53	105.66
3	"	0.05	0.12	0.02	103.3	103.49
4	"	0.05	0.13	0.03	109.64	109.85
5	"	0.05	0.15	0.01	104.91	105.12
					average	102.06
					std dev	4.31

Table 1 mass balance of ^{14}C -polydimethylsiloxane (PDMS)

After 4 months in both fresh water and salt water, <0.4% and $\leq 0.05\%$ of the total ^{14}C -poly(dimethyldiphenyl)siloxane was detected in the water and sediment, respectively. Again, >99% of the theoretical amount of ^{14}C -oil remained in the silicone topcoat (Table 2).

time (months)	system	% of total ^{14}C				
		in tin rinse	in water	in sediment	in RTV	total
1	PDMDPS fresh	0.4	0.11	0.02	103.49	104.02
2	"	0.4	0.15	0.02	94.84	95.41
3	"	0.4	0.19	0.03	102.52	103.14
4	"	0.4	0.34	0.05	94.11	94.90
1	PDMDPS salt	0.4	0.09	0.04	103.98	104.51
2	"	0.4	0.08	0.03	92.36	92.87
3	"	0.4	0.11	0.03	102.94	103.48
4	"	0.4	0.11	0.02	105.02	105.55
					average	100.49
					std dev	5.15

Table 2 mass balance of ^{14}C -poly(dimethyldiphenyl)siloxane (PDMDPS)

The data indicate that silicone oils, PDMS and PDMDPS, leach very slowly from RTV11[®]. Therefore, if any loss of biofouling release behavior were to be observed over time in such silicone paint systems, it could not be explained by loss of silicone oil from the topcoat. Retention of oils by the silicone topcoat also suggests that silicone paint systems of this type should not result in significant accumulation of silicone oils in marine and fresh water environments.

References

1. H. Brown and J. Chaudhury, *Science*, **269**, 1497 (1995)
2. G. W. Swain, J. R. Griffith, J. D. Bulman and H. Vincent, *Biofouling*, **6**, 105 (1992).

Acknowledgment

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